PB85-167922

Intramolecular Motion and Reorientational Barriers in 9-Fluorenone, 4-Methyl-9-Fluorenone and 4,5-Dimethyl-9-Fluorenone

(U.S.) Environmental Monitoring Systems Lab.
Research Triangle Park, NC

1985

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/J-85/006	2. PB85-167922
4. TITLE AND SUBTITLE: Intramolecular Motion and Reorientational Barriers in 9-Fluorenone, 4-Methyl-9-Fluorenone, and 4,5-Dimethylfluorenone (Journal Version)	5. REPORT DATE: 1985
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): Nancy K. Wilson	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Environmental Monitoring Systems Laboratory, Environmental Monitoring Division, Advanced Analysis Techniques Branch, U.S. EPA, Research Triangle Park, N. C. 27711	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS: See 9	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE: EPA/600/08

15. SUPPLEMENTARY NOTES
REF: Magnetic Resonance in Chemistry, 23(1):12-15, January 1985

16. ABSTRACT

Carbon-13 nuclear magnetic resonance spin-lattice relaxation times and nuclear Overhauser enhancements were measured as functions of temperature for the hydrogen-bearing carbons in 9-fluorenone, 4-methyl-9-fluorenone, and 4,5-dimethyl-9-fluorenone. Reorientational diffusion constants were obtained from the dipolar T_1 values. Isotropic overall molecular motion was assumed, and the methyl group rotation was separated from the overall molecular reorientation by the method of Woessner. Arrhenius plots of the dependence of the rotation rates on temperature provided values of the energy barriers for molecular reorientation and methyl group rotation. The energy barriers for molecular reorientation are essentially the same: 9-fluorenone, 11 ± 0.5 kJ/mol; 4-methyl-9-fluorenone, 11.9 ± 0.5 kJ/mol; and 4,5-dimethyl-9-fluorenone, 11.7 ± 0.2 kJ/mol. The barriers to methyl group rotation are: 4-methyl-9-fluorenone, 7.8 ± 0.9 kJ/mol, and 4,5-dimethyl-9-fluorenone, 11.0 ± 0.5 kJ/mol. Thus the bay methyl-methyl steric interaction in 4,5-dimethyl-9-fluorenone increases the methyl rotational barrier by 3.2 kJ/mol.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
steric hindrance ^{13}C nuclear magnetic resonance spin-lattice relaxation hindered rotation fluorenone		

18. DISTRIBUTION STATEMENT: Release to Publi	19. SECURITY CLASS *(This Report)*: Unclassified	21. NO. OF PAGES: 5
	20. SECURITY CLASS *(This page)*: Unclassified	22. PRICE

REPRODUCED BY NATIONAL TECHNICAL INFORMATION SERVICE U.S. DEPARTMENT OF COMMERCE SPRINGFIELD, VA. 22161

EPA/600/J-85/006
JOURNAL ARTICLE

Intramolecular Motion and Reorientational Barriers in 9-Fluorenone, 4-Methyl-9-fluorenone and 4,5-Dimethyl-9-fluorenone*

Nancy K. Wilson
Environmental Monitoring Systems Laboratory, US Environmental Protection Agency, Research Triangle Park, North Carolina 27711, USA

Carbon-13 nuclear magnetic resonance spin–lattice relaxation times and nuclear Overhauser enhancements were measured as functions of temperature for the hydrogen-bearing carbons in 9-fluorenone, 4-methyl-9-fluorenone and 4,5-dimethyl-9-fluorenone. Reorientational diffusion constants were obtained from the dipolar T_1 values. Isotropic overall molecular motion was assumed, and the methyl group rotation was separated from the overall molecular reorientation by the method of Woessner. Arrhenius plots of the dependence of the rotation rates on temperature provided values of the energy barriers for molecular reorientation and methyl group rotation. The energy barriers for molecular reorientation are essentially the same: 9-fluorenone 11.8 ± 0.5 kJ mol^{-1}, 4-methyl-9-fluorenone 11.9 ± 0.5 kJ mol^{-1} and 4,5-dimethyl-9-fluorenone 11.7 ± 0.2 kJ mol^{-1}. The barriers to methyl group rotation are 4-methyl-9-fluorenone 7.8 ± 0.9 kJ mol^{-1} and 4,5-dimethyl-9-fluorenone 11.0 ± 0.5 kJ mol^{-1}. Thus the bay methyl–methyl steric interaction in 4,5-dimethyl-9-fluorenone increases the methyl rotational barrier by 3.2 kJ mol^{-1}.

Carbon-13 nuclear magnetic resonance (NMR) spin–lattice relaxation time (T_1) measurements have been used extensively in the past decade to examine various aspects of molecular motion.[1,2] Dipole–dipole relaxation times are sensitive to rapid processes in the rate range 10^8–10^{12} s^{-1}, such as methyl group rotation. Thus relaxation methods can often provide a means of determining the relatively low energy barriers, which are inaccessible by ordinary NMR line-shape methods, for these processes. Relaxation methods for intramolecular rate measurements have been reviewed recently.[3]

Because of the r^{-6} dependence of dipole–dipole relaxation, the relaxation of hydrogen-bearing carbons is dominated by their interactions with directly attached hydrogens. Under extreme narrowing conditions, if the dipolar relaxation can be described by a single effective correlation time,[4] the rate of dipolar relaxation is given by

$$1/T_1^{DD} = n\gamma_C^2\gamma_H^2\hbar^2 r_{CH}^{-6}\tau_c \qquad (1)$$

where T_1^{DD} is the dipolar contribution to T_1, γ_C and γ_H are the carbon and hydrogen magnetogyric ratios, respectively, r_{CH} is the carbon–hydrogen internuclear distance, n is the number of attached protons and τ_c is the effective correlation time for rotational reorientation.[5] The nuclear Overhauser enhancement (NOE) depends on dipolar relaxation; hence, T_1^{DD} can be determined directly from the observed T_1 and NOE measurements using the relationship

$$T_1^{DD} = 1.988T_1/\eta \qquad (2)$$

where $\eta = \text{NOE} - 1$.

Since the internal motion of a molecule is superimposed on its overall motion, it is necessary to separate τ_c for the motion of interest from that for the overall reorientation. To isolate the methyl group rotation from the overall motion, an analysis[5] based on the work of Woessner[6,7] can be used. We assumed that, in the methylfluorenones, the overall molecular motion is isotropic and the methyl group rotates randomly about its axis in 120° jumps. A molecular rotational diffusion constant, D, can then be obtained from the mean correlation times for the aromatic carbons:

$$\tau_c = D/6 \qquad (3)$$

The rate of methyl rotation (the methyl jump rate, D_j) is then related to the methyl carbon relaxation time, T_1^{DD} (CH_3), and the molecular diffusion constant, D, by

$$1/T_1^{DD}(CH_3) = 3\gamma_C^2\gamma_H^2\hbar^2 r_{CH}^{-6}[A/6D + (B+C)/(6D+3D_j/2)] \qquad (4)$$

where A, B and C are geometric factors determined by the angle between the C—H bond vectors and the C–CH_3 rotation axis.[3,8] The quantity in brackets in Eqn (4) is the methyl correlation time:

$$\tau_c(CH_3) = A/6D + (B+C)/(6D+3D_j/2) \qquad (5)$$

where $A = 0.111$, $B = 0.296$ and $C = 0.593$ for a tetrahedral methyl group.

Thus the methyl jump rate at a given temperature

* Presented in part at the 186th National Meeting of the American Chemical Society, Washington, DC, August 28–September 2, 1983. Abstract ORGN 144. This paper has not been subjected to Agency review and does not necessarily reflect the views of the Agency.

CCC-0749–1581/85/0023–0012$02.00

can be calculated from two measured dipolar relaxation times—one determined by the overall molecular diffusion and one determined by the superposition of methyl rotation and the overall motion.

One way to quantify the methyl rotational barrier, V_0, from the T_1 data is to express the jump rate as an activation-controlled process:

$$D_i = D_{i0} \exp(-V_0/RT) \quad (6)$$

where D_{i0} is the jump rate of a freely rotating methyl group, that is, D_i when $V_0 = 0$. The barrier can be estimated at a single temperature from Eqn (6) by using

$$D_{i0} = (kT/I)^{1/2} \quad (7)$$

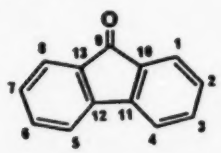
where I is the moment of inertia of the methyl group, k is the Boltzmann constant and T is the temperature. Most of the methyl rotational barriers in the literature determined from T_1 measurements have been estimated in this way.[5,9–12]

An alternative way is to perform variable-temperature ^{13}C T_1 measurements and fit the data to an Arrhenius-type equation:

$$D_i = A \exp(-E_a/RT) \quad (8)$$

where A and E_a are adjustable parameters. Although the relationship between the true three-fold barrier V_3 and V_0 is complex,[13,14] the Arrhenius activation energy E_a has been shown to approximate V_3 within a few percent for typical methyl rotational barriers.[15,16] Therefore, variable-temperature measurements should provide more accurate estimates of the true rotational barriers than those provided by single-temperature, determinations using Eqns (6) and (7).

In this study, we measured the ^{13}C T_1 and NOE values of 9-fluorenone (**1**), 4-methyl-9-fluorenone (**2**) and 4,5-dimethyl-9-fluorenone (**3**) at several temperatures. From these data we derived the energy barriers for molecular reorientation and methyl group rotation using Eqns (1)–(5) and (8).



1

EXPERIMENTS AND DATA ANALYSIS

Fluorenone was obtained commercially and its 4-methyl and 4,5-dimethyl derivatives were prepared by literature methods.[17] These compounds were examined as 0.5–1.0 M solutions in $CDCl_3$, which were degassed by four freeze–pump–thaw cycles on a vacuum line and sealed under vacuum.

Carbon-13 NMR data were obtained with a Varian XL-100-15/Nicolet TT-100 Fourier transform NMR system. Spectral widths of ±3 kHz with quadrature phase detection and 16K Fourier transforms were employed. Proton broad band decoupling at 10 W was provided by 100 Hz square-wave modulation of a single frequency centered on the ^1H spectra. Assignments of the ^{13}C chemical shifts in **1**, **2** and **3** have been reported previously.[17]

Relaxation times were measured with an inversion–recovery pulse sequence, $[-T-180°-\tau-90°-]_n$, with a 28.7-μs 90° pulse, and the waiting time between experiments T equal to at least $5T_1$. Each value of T_1 was extracted from the single-exponential decay curve of the appropriate signal S as a function of the 180°–90° pulse delay τ:

$$S = S_0[1 - 2\exp(-\tau/T_1)] + B \quad (9)$$

by three-parameter (S_0, T_1, B) least-squares fitting, where S_0 is the signal intensity at $\tau \gg T_1$ and B is an adjustable base-line constant.

NOEs were measured by comparing the integrated intensities of the peaks in spectra obtained by gating the broad band decoupler off during the long delay between pulses, and on only during data acquisition, to those obtained with continuous decoupling.[18]

All measurements were made with a 5-mm variable-temperature probe and the Varian temperature controller. The sample temperature was determined before and after each experiment with a copper–constantan thermocouple in an open liquid-filled sample tube, and the two temperatures were averaged. The temperature was controlled within ±1.5 °C over the 3-cm depth of the sample and within ±0.5 °C over the course of the experiment. From three to eight T_1 measurements were made at each temperature over the range −55 to +55 °C.

The overall isotropic rotational diffusion rates, D, and the methyl jump rates, D_i, were calculated at each temperature from the T_1 values using Eqns (1)–(5). Tetrahedral geometry ($\theta = 109.47°$) of the methyl groups, and carbon–hydrogen bond lengths of 0.109 and 0.108 nm for methyl and aromatic carbons, respectively, were assumed. The Arrhenius activation energies were then extracted from the D and D_i values as functions of temperature by linear regression analysis of $\ln D$ or $\ln D_i$ vs $1/T$ using the Bartlett method,[19,20] which allows for error in both the independent and dependent variables. Each data point was weighted proportionately to the number of independent measurements made at that temperature.

RESULTS AND DISCUSSION

The T_1 and NOE values given in Table 1 were obtained at ambient temperature. Because the spin–lattice relaxation of all of the protonated carbons is entirely dipolar, they exhibited maximal NOEs ($\eta = 1.988$) throughout the temperature range of the experiments. Their T_1 values are then directly related to the correlation times for rotational reorientation through Eqn (1). If the methyl groups were immobile, moving as the rest of the molecules to which they are attached, their T_1 values would be one third of the T_1 values of the ring carbons. If the methyl groups were freely rotating, their dipolar relaxation would be less effective than that for carbons on the molecular skeleton,

Table 1. Spin-lattice relaxation times and NOE factors at 28.7 °C

Compound	Parameter	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	CH_3
1	T_1 (s)	6.0	4.6	4.9	6.2	6.2	4.9	4.6	6.0		11.7			11.7	—
2		3.8	3.3	3.5	22.6	3.8	3.9	3.2	3.8		12.2				5.5
3		3.4	3.1	3.3	14.3	14.3	3.3	3.1	3.4		7.0	9.1	9.1	7.0	5.0
1	η	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0		1.6	1.5	1.5	1.6	—
2		2.0	2.0	2.0	1.5	2.0	2.0	2.0	2.0	0.3	0.5	1.0	1.0	0.6	2.0
3		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0		0.7	1.5	1.5	0.7	2.0

leading to long T_1 values for the methyl carbons and methyl carbon relaxation dominated by spin rotation rather than dipolar interactions. Thus the observed longer T_1 values, coupled with the measured maximal NOE values for the methyl carbons in these compounds, indicate hindered rotation of the methyl groups.

For this analysis to be valid, isotropic reorientation of the molecule as a whole is assumed. Slight motional anistropy with preferred reorientation about an axis passing approximately through C-2 and C-7 is apparent for all three compounds, and is greatest for **2**. Even in **2**, however, this anisotropy is less than 8% at 55 °C, decreases with decreasing temperature and is undetectable below 20 °C. Such apparent anisotropy will produce a contribution to the error of the experimental results that is negligible relative to the contributions of other error sources. To determine D, the average of the ring protonated carbon T_1 values was used.

The similar relaxation times for CH groups in the plane of the molecule require only that diffusion about the two in-plane axes is comparable, not that overall diffusion is isotropic. From these experiments, the effect of anisotropic motion about axes in and out of the plane on the relaxation of the methyl relative to the ring carbons cannot be determined. This does not preclude the assumption of a single effective correlation time, but is a possible contributor to the experimental error.

For very rapid rotation of methyl groups, cross-correlation of the nuclear spins can lead to non-exponential decay and, hence, erroneous T_1 values. No evidence of non-exponential behavior of the relaxation was observed here. As long as the internal diffusion rate is less than about 20 times the overall rate D, cross-correlation effects are probably small.[8,21] Although the measured rates are generally in the range where this situation obtains, the effect of possible deviations from isotropic behavior on potential cross-correlation of the $^{13}CH_3$ spin system is unknown. Therefore, zero cross-correlation is only assumed in this study.

Use of the 120° jump model is valid if the methyl jump rate is less than that for a free rotor, 8.6×10^{11} s^{-1}.[4,21,22] All the measured methyl jump rates were smaller than this, so the choice of the methyl jump over the stochastic diffusion model is reasonable.

Deviations from tetrahedral geometry may affect the calculated methyl rotational barriers, but the effects are negligibly small for ratios $T_1^{DD}(CH_3)/T_1^{DD}$ (ring) between approximately 0.4 and 2.4.[23] This ratio ranged from 1.5 to 2.1 in this study; therefore, such deviations were neglected here.

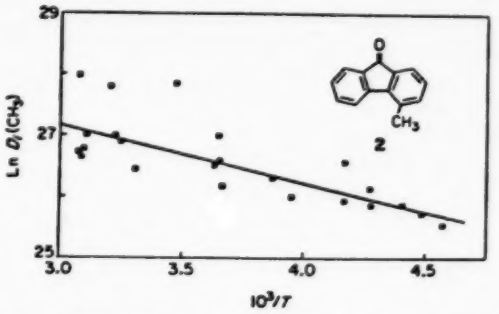


Figure 1. Arrhenius plot of the methyl 120° jump rate vs temperature for 4-methylfluorenone (**2**).

To separate the methyl reorientation from the overall reorientation becomes more difficult as the relative motion of the methyl becomes faster, because of the greater sensitivity of the dipolar relaxation rate to slower reorientational motion. In **3**, the relative rates, σ, of these reorientations are within the range 1–20, where reliable results can be obtained.[21] In **2**, however, σ is approximately 20 at high temperatures but increases to approximately 40 at low temperatures. Although each T_1 is an average of as many as eight measurements, to improve accuracy, greater errors are expected in the results for **2**. This can be clearly seen by comparing the Arrhenius plots of the methyl jump rates vs $1/T$ for **2** and **3** in Figs 1 and 2. Much more scatter is apparent for **2**.

Nevertheless, activation energies obtained from such Arrhenius plots are reasonable estimates of the methyl rotational barriers. They can be expected to be

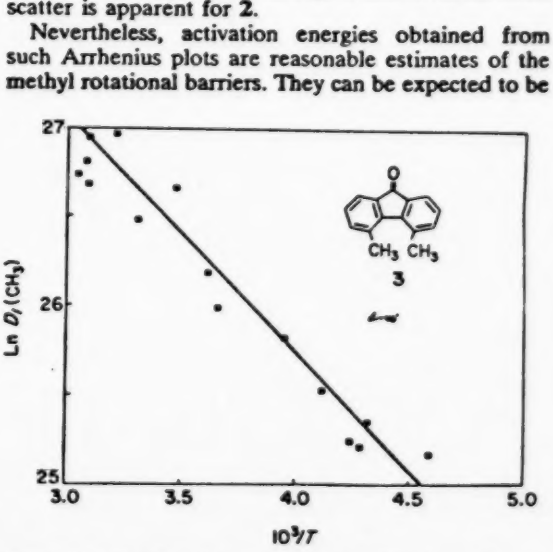


Figure 2. Arrhenius plot of the methyl 120° jump rate vs temperature for 4,5-dimethylfluorenone (**3**).

Table 2. Energy barriers for rotational reorientation

Compound	E_a (kJ mol^{-1}) Molecular reorientation	Methyl rotation
Fluorenone (1)	11.8±0.5	—
4-Methylfluorenone (2)	11.9±0.5	7.8±0.9
4,5-Dimethylfluorenone (3)	11.7±0.2	11.0±0.5

significantly more accurate than such barriers calculated from single-temperature data.[3]

The rotational barriers obtained in this study are shown in Table 2. The error ranges given are the 95% confidence intervals obtained in the Bartlett fit. Note that the activation energies for overall molecular reorientation are essentially the same, approximately 11.8 kJ or 2.8 kcal mol^{-1}, for all three compounds. This is as expected—all three molecules should have comparable overall molecular motion. In contrast, the methyl group rotational barriers are clearly different. The 4-methyl in **2** experiences a rotational barrier of 7.8 kJ mol^{-1}, whereas the 4- and 5-methyls in **3** experience one of 11.0 kJ mol^{-1}. Thus the rotation of methyl groups in both **2** and **3** is sterically hindered by interaction with the bay substituent. A bay methyl increases this hindrance by 3.2 kJ mol^{-1} over that of a bay proton through the methyl–methyl steric interaction.

Acknowledgements

Samples of 4-methylfluorenone and 4,5-dimethylfluorenone were kindly provided by J. B. Stothers. Steven T. Maher, John T. Wilson and Ruth K. Barbour provided valuable technical assistance.

REFERENCES

1. D. A. Wright, D. E. Axelson and G. C. Levy, in *Topics in Carbon-13 NMR Spectroscopy*, edited by G. C. Levy, Vol. 3, Chapt. 2. Wiley–Interscience, New York (1979).
2. J. D. Memory and N. K. Wilson, *NMR of Aromatic Compounds*. Wiley–Interscience, New York (1982).
3. J. B. Lambert, R. J. Nienhuis and J. W. Keepers, *Angew. Chem., Int. Ed. Engl.* **20**, 487 (1981).
4. L. G. Werbelow and D. M. Grant, *J. Chem. Phys.* **63**, 4742 (1975).
5. K. F. Kuhlmann and D. M. Grant, *J. Chem. Phys.* **55**, 2998 (1971).
6. D. E. Woessner, *J. Chem. Phys.* **36**, 1 (1962).
7. D. E. Woessner, *J. Chem. Phys.* **37**, 647 (1962).
8. D. E. Woessner, B. S. Snowden, Jr. and G. H. Meyer, *J. Chem. Phys.* **50**, 719 (1969).
9. J. R. Lyerla, Jr. and D. M. Grant, *J. Phys. Chem.* **76**, 3213 (1972).
10. S. W. Collins, T. D. Alger, D. M. Grant, K. F. Kuhlmann and J. C. Smith, *J. Phys. Chem.* **79**, 2031 (1975).
11. N. Platzer, *Org. Magn. Reson.* **11**, 350 (1978).
12. D. E. Axelson and C. E. Holloway, *Can. J. Chem.* **54**, 2820 (1976).
13. J. Kowalewski and T. Liljefors, *Chem. Phys. Lett.* **64**, 170 (1979).
14. H. Hervet, A. J. Dianoux, R. E. Lechner and F. Volino, *J. Phys. (Paris)* **37**, 587 (1976).
15. J. Kowalewski and A. Ericsson, *J. Phys. Chem.* **83**, 2044 (1979).
16. A. Ericsson, J. Kowalewski, T. Liljefors and P. Stilbs, *J. Magn. Reson.* **38**, 9 (1980).
17. J. B. Stothers, C. T. Tan and N. K. Wilson, *Org. Magn. Reson.* **9**, 408 (1977).
18. R. Freeman, H. D. W. Hill and R. Kaptein, *J. Magn. Reson.* **7**, 327 (1972).
19. M. V. Smith, R. W. Shaw, Jr. and R. J. Paur, *Atmos. Environ.* **17**, 65 (1983).
20. M. S. Bartlett, *Biometrics*, 207 (1949).
21. K. H. Ladner, D. K. Dalling and D. M. Grant, *J. Phys. Chem.* **80**, 1783 (1976).
22. W. Buchner, *J. Magn. Reson.* **12**, 82 (1973); **17**, 229 (1975).
23. J. W. Blunt and J. B. Stothers, *J. Magn. Reson.* **27**, 515 (1977).

Received 11 April 1984; accepted 19 April 1984

This article documents research that was conducted under the auspices of the U.S. Environmental Protection Agency (USEPA). As an arm of the government, the USEPA has a paid up, non-exclusive, irrevocable, worldwide license to reproduce, prepare derivative works, and distribute to the public all of the material contained herein, and to grant others acting on its behalf the right to do so. The USEPA grants to the National Technical Information Service, Department of Commerce, the right to act as its agent in the distribution of this material.